CONTRIBUTION TO THE THEORY OF PERMEABILITY OF MEMBRANES FOR ELECTROLYTES.

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Investigation of the permeability of membranes is most important for biology. The complicated and variable permeability of biological membranes cannot be understood before the simpler conditions in artificial membranes of different qualities have been satisfactorily explained. After M. Traube in 1867 had developed the copper ferrocyanide membrane and Pfeffer published his investigations, the prevalent interest of physicochemists was directed to the phenomenon of the osmotic pressure for many years. The problem of the permeability of the membrane has been neglected for a long time. In the last 20 years several authors have taken up this problem. R. Collander[1] has given a good review, of this subject as an introduction to his experimental work on the permeability of the Traube membrane for *non-electrolytes*. I am referring, in this paper, to some experiments on the permeability of several membranes for *electrolytes* which will be published from this laboratory in a series of papers.[2] The essential contents of these are as follows.

A. 1. The starting point of the investigation was a confirmation of the experiments of Jacques Loeb and R. Beutner[3] on the electric phenomena of the apple skin. The potential difference of the apple skin against an electrolyte solution depends on the nature and the concentration of the dissolved electrolytes. The anions have no influence at all, the cations exert an effect which depends on their

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[1] Collander, R., *Kolloidchem. Beihefte*, 1924, xix, 72.

[2] Fujita, A., *Biochem. Z.*, 1925 (in press). Michaelis, L., and Fujita, A., *Biochem. Z.*, 1925 (in press).

[3] Loeb, J., and Beutner, R., *Biochem. Z.*, 1912, xli, 1. Beutner, R., Die Entstehung elektrischer Ströme in lebenden Geweben, Stuttgart, 1920.

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valency and on their chemical nature. When varying the concentrations of a given cation, the P.D. changes by 57 millivolts for each power of ten of the concentration if the cation is univalent.

2. Michaelis and Fujita showed by direct diffusion experiments that the apple skin is absolutely impermeable for the electrolytes of the apple juice when the diffusion takes place against pure water. On the other hand an exchange of the cations occurs when the diffusion takes place against an electrolyte solution, e.g. increasing amounts of K· can be detected, from day to day, in a NaCl solution in which the apple is dipped. Anions are never exchanged.

B. When two solutions of any electrolyte in different concentrations are separated from each other by a membrane of parchment paper, the P.D. of the solutions is different from that obtained in free contact of the solutions, and that always in such a direction as though the mobility of the anion were relatively diminished in comparison to the mobility of the cation, under the influence of the membrane.

C. 1. When two electrolyte solutions are separated from each other by a membrane of collodion which has previously been thoroughly dried,[4] the P.D. of the solutions differs from that obtained without a membrane in a much higher degree than in the case of parchment paper. The P.D. depends only on the nature and the concentration of the cations. The anions are of no importance at all, and this is approximately true even for OH' ions.

2. Two solutions of one electrolyte in different concentrations being given, the potential difference for a proportion of the concentrations of 1:10 is approximately 57 millivolts for any univalent cation, that is the thermodynamically possible maximum value for a chain reversible for cations. This maximum effect is reached practically completely for the HCl concentration chain, not quite so completely for chains with neutral salts. For polyvalent cations the P.D. is smaller and inconstant, especially for bivalent ions, while trivalent ions give a more reproducible P.D. being about $\frac{1}{3}$ of the value for univalent cations.

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[4] Such a collodion bag must be dried at room temperature at least 1 day before bringing into contact with water. It is very different from the collodion bags ordinarily used for dialysis, etc.

3. In a chain consisting of two solutions of different electrolytes in equal concentration with a common cation but with different anions, the P.D. is always practically zero, even if the anions are of different valency.

4. Two solutions of different electrolytes in equal concentrations with any anion and with two different cations being given, the potential difference depends not only on the valency but also, in high degree, on the chemical nature of the cation.

5. A HCl solution or a solution of any neutral salt does not diffuse across such a collodion membrane against pure water at all.

6. When the solutions of two different electrolytes of equal concentration are separated by a collodion membrane, only the cations are exchanged by diffusion, the anions are not.

7. In opposition to that, NaOH diffuses easily against pure water, but it does not diffuse against solutions of neutral salts. This last assertion must be made with some restriction, because diffusion experiments with collodion in strongly alkaline solutions cannot be continued for a very long time. The membrane is slowly corroded in the alkaline solution in consequence of a hydrolysis of the cellulose nitrate ester. But diffusion of alkali does not seem to take place while the membrane is intact, i.e. for some days, depending on the thickness of the membrane. (In neutral or even in acid solutions a collodion bag keeps many weeks and allows us to extend the diffusion experiments indefinitely.)

In the course of the following theoretical discussion more details of the experiments will be given.

D. 1. As an attempt to interpret all of these facts the hypothesis may be made that the mobility of the anions in the capillary canals within the membrane is much more inhibited than that of the cations. In parchment paper the mobility of the anions is diminished in comparison with that of the cations; in the apple skin and in collodion it is practically annulled.

This, in connection with some auxiliary hypotheses, is the foundation of the following theoretical discussion.

2. Two circumstances may be recognized to be effective for the alteration of the ionic mobility in capillary spaces. The first is the hydration of the ions. Any ion drags a water envelope when

moving through the water.   The attraction of the ions for the water molecules may be interpreted as an electrostatic attraction of the ion to the electric dipole represented by the water molecule.   The dipoles are oriented in a wide extent round the ion as to the direction of their axis and constrained in their local distribution; this effect decreases with the distance from the ion.   When an ion moves in a capillary canal, the frictional resistance is increased, if the sphere of attraction to the water molecules extends to those water molecules which by adhesion are fixed to the wall of the canal.

The second matter is the fact that the walls of the canal are generally covered with an electric double layer.   The retardation of any anion in parchment paper and collodion may be supposed to be the consequence of the negative charge of these membranes in aqueous solutions.   Amphoteric membranes the charge of which can be changed by varied hydrogen ion concentration may show a quite different behavior.   In all events this effect of the capillaries, the conditions being given, is always directed either only to the anions or only to the cations.

3. At this place it seems to me to be important to insert a discussion of the charge of the walls.   We have been considering collodion as a membrane which is always negative.   In fact the investigations of Perrin,[5] Gyemant,[6] and of Jacques Loeb[7] prove that collodion (unless it is impregnated with proteins) is never positively charged, not even by strong acids.   At the most it is discharged by strong acids.   However, the impermeability of collodion for anions is evident even in HCl solutions.   The potential difference of collodion against HCl solutions being almost zero, as experiments on electric endosmosis show, seems to be in contradiction to the interpretation just given.   Yet this contradiction is only apparent.   Collodion has the faculty of adsorbing negative ions even in acid solutions.   However, in high hydrogen ion concentrations the distance of the fixed negative ion layer from the opposite hydrogen ion layer[8] is so

[5] Perrin, J., *J. chim. phys.*, 1904, ii, 601; 1905, iii, 50.

[6] Gyemant, A., *Kolloid-Z.*, 1921, xxviii, 103.

[7] Loeb, J., *J. Gen. Physiol.*, 1923–24, vi, 105.

[8] This layer is not a plane, but of a certain thickness or "diffusity" according to Gouy (Gouy, M., *J. Phys.*, 1910, ix, 457).   For certain calculations one may

small that the potential difference of the double layer approximately vanishes. For this P.D. not only the density of the electric charge but also the distance of the layers is important. The smaller the distance, the smaller is the P.D. The electrical density of the layer is evidently of importance for the influence on the ionic mobility. It is not necessary that the number of the negative ions adsorbed by the square unit, i.e. the electrical density of the layer, be smaller in presence of HCl than in presence of KCl. In so far we may consider collodion to be negatively charged even in HCl solutions. One must distinguish clearly between the density and the P.D. of the double layer.

4. The mechanism of the retarding effect of the electric charge of the wall may be represented by a scheme already suggested by Bethe and Toropoff[9] in order to explain the deviations from the neutral reaction on either side of a membrane in an orginally neutral solution when an electric current flows across the membrane. If the wall is negative this charge can only be brought about by adsorbing negative ions. These ions appertain to the electrolyte solution or are the OH' ions of the water. Therefore, there must be a lack of anions in the movable liquid within the canal. The mobility of the anions observed in the experiments is an average value of the different mobilities of the fixed and the free anions. Even if the mobility of the *free* anions were wholly unchanged, yet the average value of the anions would be diminished. Furthermore, if the canal is narrow enough, it may happen that all of the anions are fixed by the wall and only cations can move. Let us admit this to be true for the membrane of previously dried collodion, which is practically impermeable for any anion. This membrane is an excellent model for the apple skin and even for the membrane of the red blood corpuscles with the difference that the membrane of the blood corpuscles is permeable for anions and impermeable for cations from which fact we may possibly infer that this membrane is positive under physiological conditions.

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imagine a real plane by assuming that all of the positive ions are in one plane, at the distance of the electric center of gravitation from the wall. This imaginary layer of positive ions is meant here.

[9] Bethe, A., and Toropoff, T., Z. *physik. Chem.*, 1914, lxxxviii, 686; 1915, lxxxix, 597.

However, the permeability of the physiological membrane such as the one of a blood corpuscle is a much more complicated problem as this membrane has a permeability varying according to the conditions. We should start the study on permeability from such membranes as collodion, the permeability of which depends on the conditions of the surrounding solution as little as possible. The amphoteric nature of physiological membranes is an impediment for the recognition of the fundamental facts, just as the complicated behavior of the dissociation of amphoteric electrolytes cannot be the starting point in the investigations of electrolytes. Some papers from Hoeber's laboratory[10] show that the electric phenomena in amphoteric membranes or diaphragms such as gelatin are altered by a change of pH. The physiological importance of this fact is evident but it is an impediment for the fundamental investigations on ionic permeability. For this purpose such membranes are preferable which do not change the sign of charge with varying pH.

The above hypotheses on the causes which bring about the retardation of ions and especially of the ions of one sign of charge cannot yet be proved quantitatively. Therefore it is not certain that there may not be other factors besides those mentioned. The following treatment is independent of such considerations. From now on let us merely assume that there is a relative retardation of the mobility of the anions. We shall then discuss the phenomena to be expected as a consequence and compare them with the experimental results obtained in the papers quoted.

5. Let the mobility of the cation and of the anion of an electrolyte in a free aqueous solution be U and V and let these mobilities be within the membrane u and v on the average. The further development of the theory is different for "*permeable*" membranes where u and v have finite values and for "*semipermeable*" membrane where one of these values vanishes. A transition is represented by cases where the permeability for one kind of ion is so strongly decreased that the membrane appears as a semipermeable one in experiments of short duration, but as a permeable one in experiments of a long duration. Such cases may be treated after the one or the other

[10] Mond, R., *Arch. ges. Physiol.*, 1924, cciii, 247. Höber, R., *Z. physik. Chem.*, 1924, cx, 142.

theory according to the time of observation. In the transition time there will be a little indefiniteness in the interpretation. In practice no difficulty has occurred hitherto. The membranes of our experiments were either permeable for any ion in a measurable degree or they were practically impermeable for any anion. But transition cases may also be met.

A. Theory for Permeable Membranes.

6. Let a permeable membrane separate two solutions of the same electrolyte of different concentrations c_1 and c_2. Then a *quasistationary condition* will soon be established. Suppose the concentration within the aqueous solutions is maintained practically constant by convection, *i.e.* by stirring or shaking, a fall of concentration is formed by the diffusion which linearly falls from c_1 to c_2 from one boundary of the membrane to the other. For such a case the P.D. of the two solutions is simply a liquid junction potential and can be calculated after the well known formula

$$E = 0.057 \cdot \frac{\frac{u}{w} - \frac{v}{\bar{w}}}{u + v} \log \frac{c_1}{c_2} \text{ volts} \tag{1}$$

where u and v are the mobilities of the cation and the anion within the membrane and w and $\bar{w}$ are the valencies of the cation and the anion. The observed P.D. therefore enables us to calculate the mobilities of the ions in the membrane, at least relatively to each other. From (1) it follows, if $c_1 : c_2 = 10:1$,

$$\frac{u}{v} = \frac{0.057 + E\bar{w}}{0.057 - Ew} \tag{2}$$

Let us perform the calculation for one of the parchment paper membranes above mentioned—the results being fairly reproducible for one sample of membrane but different for different samples—and note the results in the following table:

	KCl	KBr	KI	K_2CO_3	$K_2C_2O_4$	NH_4Cl	NaCl	LiCl	$CaCl_2$
$\frac{u}{v}$ (membrane)	1,6	1,8	1,6	1,3	3,3	1,5	1,2	1,07	1,38
$\frac{U}{V}$ (free diffusion)	0,98	0,95	0,97	1,07	1,03	0,98	0,67	0,39	0,78

	BaCl₂	MgCl₂	AlCl₃	CeCl₃	K₂SO₄	K₃ferricya-nide	NaOH	HCl
$\frac{u}{v}$ (membrane)	1,25	1,17	1,14	1,11	2,56	3,45	0,65	6,3
$\frac{U}{V}$ (free diffusion)	0,84	0,69	0,61	0,86*	0,68	1,17*	0,25	4,8

The upper line contains the values of $\frac{u}{v}$ calculated from the experiments, the lower line gives $\frac{U}{V}$ for free diffusion calculated after the values of ion mobilities according to Kohlrausch and Heydweiller. The figures designated by an asterisk are taken from our own measurements in the quoted paper, determinations not being available in the literature. The calculations are not completely exact. First the mobilities depend a little on the concentration, secondly we should use the ratio of the activities of the ions instead of the concentr tiors. However, regarding the limits of error and the fact that the figures depend on the parchment paper bag used and are not of general application, any attempt at correction seems to be unnecessary. The general results are nevertheless evident. From these figures we may calculate the relative mobility of the cations, the mobility of potassium being taken as 1:

		Na	NH₄	Li	1/2Ca	1/2Ba	1/2Mg	2/3Al	1/3Ce	H
u (membrane)	1	0,74	0,93	0,56	0,86	0,77	0,73	0,71	0,69	3,9
U (free diffusion)	1	0,65	0,99	0,52	0,79	0,83	0,70	0,62		4,9

In the following table the relative mobilities of the anions are noted. The upper line gives the mobility, the mobility of potassium taken as 1, the second line gives the mobility of the anions, the mobility of chlorine taken as 1, the last line is the mobility in the free diffusion, the mobility of potassium taken as 1. A special calculation taking the mobility of chlorine as 1 is unnecessary in the case of free diffusion, the mobility of K and Cl being practically equal.

	Cl	Br	I	$\frac{1}{2}CO_3$	$\frac{1}{2}CO_4$	$\frac{1}{2}SO_4$	$\frac{1}{3}$ Ferro-cyanide	OH
v, for $u_{K^+} = 1$ (membrane).	0,62	0,55	0,62	0,33	0,33	0,39	0,41	1,5
v, for $u_{Cl^-} = 1$ (membrane).	1,0	0,9	1,0	0,53	0,53	0,63	0,86	2,4
V (free diffusion).	1,01	1,03	1,03	1,1?	0,98	1,05	?	2,7

As we see from this table, the relative alterations of the cation mobilities are very small and may perhaps not surpass the limits of error. In opposition to that the mobilities of the anions relative to each other are much more altered, in so far as the mobility of the bivalent anions is much more decreased than that of the univalent anions. In general anions suffer a relative loss of mobility in the membrane as compared with cations.

7. On the other hand such measurements may be used for *characterizing a sample of parchment paper or generally of an ultrafilter*. The simplest method for this purpose is the measurement of the P.D. of a chain with 0.1 M and 0.01 M KCl, as here the junction liquid potential in free contact is zero. The potential itself or the value of the $\frac{u}{v}$ calculated therefrom, or the transport number of the anion, calculated from that in the usual manner, may be used as an index of the quality of the membrane. The material of the membrane being given, the relative retardation of the anion, is a scale for the size of the pores. The smaller the pores the greater is the retardation of the anions. For the retardation of the anions is an average value, and the smaller the size of the pores the greater is the surface of the walls of the pores and the amount of anions fixed by the wall. Membranes of different material cannot be compared by this method, as the amount of the fixed anions depends on the specific nature of the membrane itself. According to some previous experiments with some materials used for ultrafiltration and for the filtration of bacteria, the potential of the KCl chain seems to be rather small. Greater values of this potential appear only in membranes of such a small size of pores as no longer to be fit for filtration at a reasonable speed.

B. Theory for Semipermeable Membranes.

8. The prototype of what we will call a *semipermeable* membrane is dried collodion or apple skin, both of which are permeable for any cation and impermeable for any anion. The theory is simple only for one case, *viz.* for the chain of two solutions of an acid in different concentrations. Out of our experimental material this condition is given in the chains with HCl solutions of different concentrations. The simplicity of the theory for this case consists in the fact, that the cation of this electrolyte is present in the liquid of the membrane by itself. This cation is the hydrogen ion of the water within the membrane. Even if no HCl penetrates into the membrane the water itself contains this cation. An electric current which passes the chain is conducted across the membrane by the hydrogen ions even if we admit the OH' ions to be immovable within the membrane. Let us designate the concentration[11] of the hydrogen ions in the two aqueous solutions by H_1 and H_2, and within the membrane by H_m. After 96540 = F coulombs have passed the chain, 1 mol of H ions is transferred from the one solution to the other. From this it follows, according to the usual thermodynamic considerations that the E.M.F. of the chain is

$$E = \frac{RT}{F} \cdot \ln \frac{H_1}{H_2} = 0{,}057 \cdot \log^{10} \frac{H_1}{H_2} \text{ volts at } 15°C.$$

the more dilute solution being positive. This result is almost perfectly confirmed by the experiment. In the following table the first column notes the molal concentration of the two HCl solutions of the chain, the second column gives the activity of the H ions according to the figures of Lewis and Randall, the third column gives the potential difference calculated, from these figures, and the last column is the observed P.D. for a temperature of 17°.

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[11] Here as elsewhere in this paper, unless the contrary is expressly noted, concentration means the thermodynamic concentration or the activity reduced to an aqueous solution, *i.e.* the concentration multiplied by an activity factor, which is 1 for infinitely dilute solutions in free (not in a capillary-enclosed) water, and which is of such a magnitude that the concentration when corrected by it, is always proportional to the molal-free energy. See Lewis, G. N., and Randall, M., Thermodynamics, New York, 1923.

Concentration of HCl.	Activity.	P.D. calculated.	P.D. observed.
0,1:0,01	0,0814:0,00924	54,0	54,8
0,1:0,001	0,0814:0,000984	106	108

9. The case of the dissolved electrolyte being a neutral salt may be treated as follows. Let a KCl solution be brought in contact with a collodion membrane completely dried and then thoroughly wetted with water. A diffusion will start and K· ions will penetrate but Cl′ ions will not. Therefore K· cannot be present within the membrane in the form of KCl but only of KOH. On the other hand HCl arises in the aqueous solution, the H· ions of which have migrated from the membrane in exchange with the K· ions which have penetrated into the membrane. But while in the aqueous solution this HCl easily can be diluted to a vanishing concentration by diffusion and convection, this is not the case for the KOH in the membrane, as shaking and stirring do not bring about any convection in the membrane. A concentration fall of KOH is formed in the membrane. In any cross-section of the membrane the sum of the (true) concentrations of K· and H· ions is equal to that of the OH′ ions. The OH′ ions are immovable within the membrane. The local concentration of the OH′ ions can only be varied by an alteration of the dissociation of the water, the product of the H· and OH′ concentration always remaining constant. The progress of the diffusion consists, in the region of the concentration fall, of the K· ions moving on across the membrane, while the K· concentration keeps constant from the boundary of the membrane to the beginning of the region of the gradient and is, up to this region, in a thermodynamical equilibrium with the aqueous solution. But it does not follow that the K· concentration in the free water is equal to the one in the boundary layer of the membrane, not even the thermodynamic concentration. The K· concentration in the membrane which is in equilibrium with the K· concentration of the free solution may be calculated in the following manner which is similar to the method of calculating the Donnan equilibrium. An exchange of H· and K· ions takes place at this boundary. In the equilibrium the maximum work of the

exchange of δn mols H ions and K ions vanishes. The sum of the work done in this exchange is

$$\delta n \cdot RT \cdot \left(ln \frac{K_e}{K_i} - ln \frac{H_e}{H_i} \right)$$

where K and H are the concentrations of the K˙ and the H˙ ions, and the indices e and i refer to the outside free solution and the inside solution in the membrane. Therefore, in the case of equilibrium

$$\frac{K_e}{K_i} = \frac{H_e}{H_i} \tag{1}$$

It will be practically always realized that the concentration of the free aqueous solution is kept constant by convection. Then the equilibrium is ruled by the following equations.

a) $K_e = $ constant
b) $H_e = $ constant
c) $K_e \times H_i = K_i \times H_e$
d) $K_i + H_i = OH_i$
e) $H \times OH = k_w$ $\tag{2}$

where k_w is the ion product of the water. Hence:

$$K_i{}^2 = \frac{K_e{}^2 \cdot k_w}{H_e \ (K_e + H_e)} \tag{3}$$

In a neutral solution H_e may be neglected against K_e and hence

$$\frac{K_i}{K_e} = \sqrt{\frac{k_w}{H_e}} \tag{4}$$

If the aqueous solution is neutral $(H_e = 10^{-7}; K_w = 10^{-14})$:

$$\frac{K_i}{K_e} = 10^{-3.5}$$

From that it follows that the K concentration in the membrane is much smaller than in the aqueous solution with which the equilibrium is established. The obtained figure is, however, only a rough approximation, for in equation $(2, d)$ the concentrations are the true concentrations, in the other equations (2) the concentrations mean activities. These may be different from the true concentra-

tions in the capillary spaces of the membrane in a much higher degree than in the free aqueous solution.

Furthermore it follows that there must be an electric potential difference at the boundary of the membrane, which compensates the lack of osmotic equilibrium. A few extra $K^{\cdot}$ ions penetrate into the membrane without being electrically compensated by any anions, and a few extra $H^{\cdot}$ ions move from the membrane into the aqueous solution, in such an amount as to produce the P.D.:

$$E = \frac{RT}{F} \cdot ln \frac{K_e}{K_i} = \frac{RT}{F} \cdot ln \frac{H_e}{H_i} \tag{5}$$

Substituting the value of K_i from equation (4):

$$E = \frac{RT}{2F} ln \frac{H_e}{k_w} \tag{6}$$

It may be recognized from this equation that the P.D. depends neither on the nature nor on the concentration of the cation provided it is univalent. When two different electrolyte solutions of any concentration let the cations be common or not, if only univalent, touch the two sides of the membrane, and when in addition the $H^{\cdot}$ concentration on either side is small in comparison to the concentration of the other cation, the two potential differences of either membrane boundary compensate each other. The diffusion potential within the membrane is left as the only electromotive force of the chain. Therefore in the following discussion these potentials at the membrane limit will no longer be mentioned and the diffusion potential will be considered as the only electromotive force, as far as the conditions allow it.

Suppose the immobility of the anions is not absolute but only relative as compared with the mobility of the cations, the case would be a little changed, in the following manner. When a solution of KCl is just being brought into contact with the membrane, the penetration of the $K^{\cdot}$ ions can either be accompanied by a simultaneous penetration of Cl' ions, or by an exchange of $H^{\cdot}$ ions. At the beginning, the exchange of $K^{\cdot}$ and $H^{\cdot}$ ions will prevail and the considerations just represented are valid. By and by the OH' ions within the membrane are replaced by Cl' ions, and then $K^{\cdot}$ is in the membrane

no longer in the form of KOH, but of KCl. Then no potential difference is established at the membrane boundary at all.

Let us consider a chain consisting of two solutions of different concentrations of one electrolyte touching the two sides of a membrane. In the first stage of the diffusion there will be a very small concentration of the cations within the membrane, the ratio of these concentrations on the two sides being the same as in the aqueous solutions. There will be a P.D. at either membrane boundary but these cancel each other. In a later stage of the diffusion there will be on either side within the membrane the same cation concentration as in the adjacent aqueous solution and no boundary potential difference. The ratio of the cation concentrations on the two sides within the membrane being the same in either stage, the diffusion potential within the membrane is the same in either case. The boundary potentials are without effect in either case. In the transition time it may occur that the boundary potentials do not cancel each other exactly, but then also the diffusion potential is altered in the opposite sense. These two effects though not exactly calculable will at any case approximately cancel each other. The electromotive force of the whole chain will practically remain unchanged in the different stages of the diffusion. Therefore, when calculating the electromotive force of such a chain, we may restrict ourselves to the case of a complete impermeability for anions.

In Fig. 1 *AB* is the direction of the diffusion. Let *C* be the boundary of the solution against the membrane, on the left side the free water, on the right the membrane. Let *AD* represent the concentration of the K ions in the water. When entering the pores of the membrane this concentration rapidly decreases down to *F*. However, the line *EF* does not represent a fall of diffusion but a state of equilibrium. The concentration keeps constant from *F* to *G*, *GH* represents the fall of diffusion which decreases down to zero at *H*. The progress of the diffusion consists in the localization of this fall being pushed forward so as to represent the line *IB* some time later. The concentration of the H· ions is shown only for the region on the right of *M* as a dotted line and on an exaggerated scale. This concentration is very small and constant between *M* and *N* and then gradually increases to a constant value (*L*) in the

interior of the membrane. The diffusion fall gradually moves on and reaches the opposite side of the membrane. Experience teaches that this process takes at least a day in a membrane of 0.1 mm. of thickness at most. If the P.D. of the aqueous solution and the membrane is to be calculated, the method is different according to whether we take the time when the diffusion fall still exists within the membrane or when the diffusion has already reached the opposite boundary of the membrane. The second case is easier for the theoretical treatment.
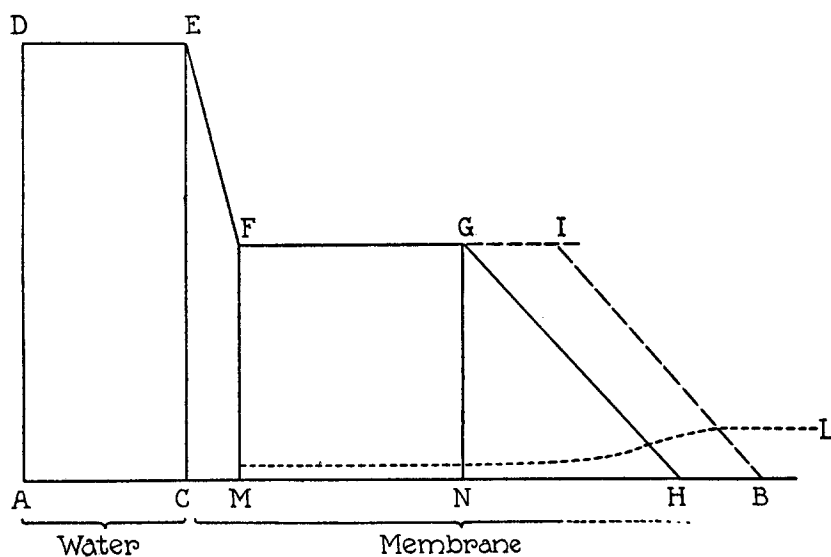

Fig. 1.

10. Let us suppose the membrane to be in contact with two KCl solutions of different concentrations, the diffusion having already penetrated across the membrane completely. Then there is on the one side within the membrane a constant $K^{\cdot}$ concentration which is in equilibrium with the one aqueous solution, and on the other side within the membrane there is some other constant $K^{\cdot}$ concentration which is in equilibrium with the other solution, and there is a quasi-stationary concentration fall of the $K^{\cdot}$ concentration somewhere between these two regions. When δ $n \cdot F$ coulombs pass the cross-section the change of condition consists in δ n mols of $K^{\cdot}$ ions being

transferred from one side of the membrane to the other in a reversible manner. K˙ and H˙ ions are transferred on the one side from the water into the membrane and on the other side inversely, too, but this transport takes place without doing or requiring any work, since equilibrium is established. The two K˙ concentrations within the membrane, according to (4), have the same proportion to each other as the two K˙ concentrations of the two aqueous solutions, provided the H˙ concentration in the two aqueous solutions is kept constant. Hence the osmotic work of the transport is $= RT \cdot ln \dfrac{K_1}{K_2}$ where K_1 and K_2 are the K concentrations of the two aqueous solutions. Hence results the P.D.

$$E = \frac{RT}{F \cdot w} \cdot ln \frac{K_1}{K_2}$$

This holds for cations of any valency if w is the valency.

However, since the establishment of this quasistationary condition takes much time, we face, as a rule, another condition when measuring the P.D. We may designate it as a *prequasistationary condition*. On either side within the membrane a condition is established such as in Fig. 1 and the P.D. is composed of the P.D. between the one boundary layer of the membrane and the inside of the membrane which do not yet contain any K˙, and the corresponding P.D. on the other side within the membrane. We should calculate these two P.D. separately. Either is a diffusion potential between a KOH solution and pure water. There are two methods of calculating such a diffusion potential. If the two solutions touch each other without being mixed by any shaking but only by a pure diffusion, the Planck[12] formula holds. If there is a gradual transition of the two solutions such as may be produced by gradually mixing the two liquids, the Henderson[13] formula holds which is much more practicable than the other one. In our case neither condition is given. The fall of the K˙ concentration is produced by a diffusion but the fall of the OH′ ions is not produced by any movement at all but by a local variation in the dissociation of the water. So we

[12] Planck, M., *Ann. Physik u. Chem.*, 1890, xl, 561.

[13] Henderson, P., *Z. physik. Chem.*, 1907, lix, 118.

should calculate the potential by a new method. The conditions
being exactly given the differential formula may be easily established.
Let us cut out a very thin layer by two cross-sections through any
part of the region of the fall and let us calculate the concentration
of the K· and the H· ions in it. We may suppose the fall of the K·
ions to be linear, but then the fall of the OH' ions is not linear. We
may find out an available function for the OH' fall by means of the
relations developed above. Supposed the mobility of the K· and
the H· ions in the membrane to be known, we may calculate the
participation of the K· and the H· ions in the conduction of an electric
current. Hence we may calculate the osmotic work of the trans-
port of these ions into the neighboring layer by the current. This
work divided by F is the p.d. of the neighboring layers. It repre-
sents a differential which has to be integrated from the beginning of
the diffusion fall to the end in order to obtain the total p.d. How-
ever, the integration of this equation meets scarcely surmountable
mathematical difficulties. We should renounce an exact solution
of this problem.

But it is evident that the difference of the e.m.f. of the chain is but
little different whether the *prequasistationary* condition or the *quasi-
stationary* condition is established. The difference can only be of
the magnitude of a correction, an estimation of which may be possible
if we represent the structure of the diffusion fall by a somewhat
inadequate supposition such as to facilitate the calculation. Let us
suppose both the fall of the K· ions and the H· ions to be linear,
then the system is fit for the application of the Henderson formula.
Let us calculate by this method the potential between a KOH solu-
tion and pure water. Let the concentration of the KOH solutions
be K, the H· concentration of the pure water H. Let the mobility
of the K· ions be u, the one of the H· ions y, the one of the OH' ions
zero, according to their immobility in the membrane. Hence the
p.d. results:

$$E = \frac{uK - yH}{uK + yH} \cdot \frac{RT}{F} \cdot ln \frac{u \cdot K}{yH}$$

The difference of the two p.d.'s, the K· concentration on the two
sides being K_1 and K_2, amounts to

$$E_1 - E_2 = \frac{uK_1 - yH}{uK_1 + yH} \cdot \frac{RT}{F} \cdot ln \frac{uK_1}{yH} - \frac{uK_2 - yH}{uK_2 + yH} \cdot \frac{RT}{F} \cdot ln \frac{uK_2}{yH}$$

But we may without hesitation neglect $y \cdot H$ against $u \cdot K_1$ and $u \cdot K_2$. Then approximately

$$E_1 - E_2 = \frac{RT}{F} \cdot \ln \frac{K_1}{K_2}$$

This is the same formula as in the quasistationary condition. In fact, experience teaches that the potential in a freshly prepared collodion bag which has just been brought into contact with the electrolyte solutions is equal to the potential after the contact has been extended to many days. The differences are not greater than the reproducibility of such chains generally allows; *i.e.*, within a few millivolts.

From this it follows that we may calculate the potential difference of a really semipermeable membrane in the same manner as that of a permeable by considering the mobility of any anion to be zero. The difference of the two cases is the following: In a permeable membrane there is no potential difference between either aqueous solution and the neighboring layer of the membrane. The only electromotive force of the chain is the diffusion potential. In a really semipermeable membrane there is besides this diffusion potential a potential difference at either membrane boundary. ~~But provided the H'-concentration of the aqueous solutions is kept constant by stirring or convection, these two boundary potentials cancel each other, and the diffusion potential within the membrane remains the only electromotive force of the chain.~~ Probably a semipermeable membrane is never realized in the exact meaning of the word, the impermeability of the anions may always be only relative when compared with the one of the cations. If that be the case the conditions at the boundary may be represented as follows: When a KCl solution is brought into contact with an approximately semipermeable membrane, first of all an exchange of K˙ ions of the solution and of H˙ ions of the membrane starts. This exchange can go on only to a very small extent as we have shown above. A very small concentration of K˙ ions within the membrane is in equilibrium with a high concentration in the water. Gradually also chlorine ions may immigrate into the membrane and by and by the K˙ concentration in the membrane is increased also. But the permeability of the chlorine ions is so extremely small that under ordinary experi-

mental conditions probably equality of the salt concentration without and within the membrane is never reached. However, the potential difference of the membrane chain as a whole is practically independent of the progress of the very slow process of the diffusion.

11. The experimental test of the theory of the potential with neutral salt solution showed the following. The P.D. of a concentration chain with KCl or any other neutral salt is reproducible and constant within a few millivolts for each collodion bag. There is no difference between the P.D. immediately after the installation of such a chain and after the contact has continued for many days. The P.D.'s are somewhat individual for each bag. The maximum value in KCl or other salts with univalent cation is about 52 millivolts; in many cases the P.D. is about 45 millivolts, only seldom much less. The thermodynamic activities in 0,01 and 0,1 M. solutions of KCl are in the proportion of $0,00890:0,0745 = 1:8,35$. Therefore a P.D.'s of 52,5 millivolts at 15° Celsius may be expected. This is just the maximum value in our experiments. The fact that some smaller values often occurred may be interpreted by admitting such bags to be a little more permeable for anions. As we shall see such a permeability for anions is rarely found in direct diffusion experiments. Therefore, we may think also of the possibility that the potential is not quite exactly established according to the thermodynamical equilibrium. The fact that the P.D. is not quite so reproducible and constant as in metallic galvanic chains may favor such a hypothesis. At all events the anion of the neutral salt is quite indifferent, even if it be polyvalent. The following table gives some of the experimental results of our quoted paper:

Concentration Chains, 0,1:0,01 M Solutions.

	Some individual P.D.'s	Average P.D. of all experiments.
KCl	46, 43, 49, 56, 48	46,7
KI		47,5
KBr		44,7
KNO_3		45
K_2SO_4		43,6
K_2CO_3		48
$K_2C_2O_4$		47,5
K_3FeCy_6		49

12. The only concentration chains which, as a rule, do not completely reach the expected value are some concentration chains with KOH and NaOH. In KOH the deviations are not considerable, sometimes even 45 millivolts being reached. In NaOH the values are still smaller, on the average 34 millivolts, and there is besides an evident inconstancy of the potential. The cause may be that the OH ions though not very mobile are nevertheless more mobile than other anions and, therefore, the mobility of the OH' ion may not completely be neglected, if there is a relatively slow cation. As we shall show later, the mobility of Na· in the membrane is very much smaller than the one of K·. This may be the cause of the fact that the concentration chains with KOH as a rule give higher potentials than the chains with NaOH.
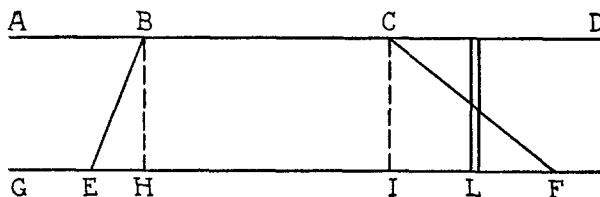

Fig. 2.

C. Theory of Chains With Semipermeable Membranes and Solutions of Different Electrolytes in Equal Concentrations.

13. Let two electrolyte solutions of equal concentration but with different cations be in contact with the two sides of a membrane impermeable for anions. Let us calculate the p.d. for the case that the *prequasistationary condition* is established. We have to discriminate between two stages of the diffusion process, the time before the two regions of the concentration fall have touched each other, and the time after these regions having met and crossed. The second case is easier, because in this case there is no intermediary region of pure water and the participation of the H· ions in conducting an electric current may be neglected. The concentration fall within the membrane is symbolized in Fig. 2. The abscissa is the direction of the diffusion. *ABCFH* is the concentration of the one cation and *DCBEG* is the concentration of the other cation. Let δ *n·* F coulombs pass the cross-section. Osmotic work is done only between

E and H, and between I and F, since only here there is a concentration fall. Let us imagine a very thin layer cut out by two cross-sections through the one of these two regions, as hinted in Fig. 2, at L. Let both cations be univalent. Let the concentration of the one cation in this thin layer be c_1, the concentration of the other cation c_2. The first cation participates in the transport of the current with the fraction $\dfrac{u_1 c_1}{u_1 c_1 + u_2 c_2}$, the other cation with the fraction $\dfrac{u_2 c_2}{u_1 c_1 + u_2 c_2}$, where u_1 and u_2 are the mobilities of the cations in the membrane. Then the osmotic work in transferring F coulombs in a neighboring cross-section layer is

$$d A = \frac{u_1 c_1}{u_1 c_1 + u_2 c_2} RT \frac{d c_1}{c_1} - \frac{u_2 c_2}{u_1 c_1 + u_2 c_2} RT \frac{d c_2}{c_2}$$

The second member of the right side is 0, as $dc_2 = 0$. Let the fall of diffusion be linear, then.

$$c_1 = C_1 \left(1 - \frac{x}{D_1}\right)$$

where C_1 is the concentration of the first cation in the membrane which is in equilibrium with the adjacent aqueous solution, x the distance of the cross-section from the beginning of the region of the diffusion fall, and D_1 is the total longitudinal extent of this fall. Putting this value for c_1, intergrating the work over the total longitudinal extent of the diffusion fall from $x = 0$ to $x = D_1$, the total work results:

$$A_1 = RT \cdot \int_0^{D_1} \frac{u_1 C_1 \left(1 - \frac{x}{D_1}\right) \cdot dx}{\left[u_1 C_1 \left(1 - \frac{x}{D_1}\right) + u_2 C_2\right] (D_1 - x)}$$

If

$$C_1 = C_2,$$

$$A_1 = - RT \cdot \ln \frac{u_1}{u_1 + u_2}$$

Likewise for the other region of diffusion fall:

$$A_2 = RT \ln \frac{u_2}{u_1 + u_2}$$

Hence the total work

$$A = A_1 + A_2 = RT \cdot ln\frac{u_2}{u_1}$$

and the P.D.:

$$E_1 - E_2 = \frac{RT}{F} \cdot ln\frac{u_2}{u_1}$$

The P.D., therefore, does not depend on the concentrations of the two cations, provided the two concentrations are the same, but only on the mobilities of the two cations. We therefore arrive at the result that the P.D. can be very little different from that when the two regions of the diffusion fall have not yet met and are still separated by a region of pure water.

We may assume the membrane either to be completely impermeable for anions or only relatively impermeable for them. In the first case the cation concentration of the membrane layer adjacent to the aqueous solution, the pH being given, is independent of the nature of the cation provided it is univalent, and depends only on the concentration in the aqueous solution. This holds for either side of the membrane. If the concentration of the cation in one aqueous solution is the same as the other cation in the other solution, the cation concentrations on either side within the membrane are also equal. Therefore, the given formula may be applied for the calculation of the diffusion potential within the membrane. The boundary potentials cancel each other. If the membrane is only *relatively* impermeable for anions, the same only holds at the very start of the diffusion process. After the diffusion has gone so far that the concentrations of the salts in either of the aqueous solutions and the adjacent membrane layers have become equal, the cation concentrations on either side within the membrane are again equal and the given formula for the calculation of the diffusion potential within the membrane may be applied again. In this case there is no boundary potential at all. In the intervening time it may happen that the diffusion process on the one side at a given time has advanced further than on the other side, if the mobilities of the cations are different from each other. In this case an exact calculation becomes difficult. First, the concentrations of either cation on both sides

within the membrane may be different and the given formula for the calculation of the diffusion potential is no longer valid; on the other hand the two boundary potentials no longer cancel each other. It may be supposed that these two factors which may alter the total potential difference compensate each other approximately. Furthermore experience teaches that the P.D. of such a chain does not practically vary from the very start of the experiment for several days, at least not more than such chains usually vary, within a few millivolts, while the total value of such chains sometimes reaches between 100 and 200 millivolts. We are allowed, therefore, to consider the electromotive force of such chains as a consequence of the different mobilities of the cations, and apply the given formula to calculate the ratio of the mobilities of the two cations from the electromotive force by this formula. If one or both of the two cations are not univalent the calculation for the diffusion potential becomes more difficult and in addition the boundary potentials do not cancel each other. Let us restrict ourselves to univalent cations.

14. If we know the P.D. of a chain of two solutions of electrolytes with any anion and with two different univalent cations in equal concentrations we can calculate the relative mobilities of these two cations in the membrane. If we perform this calculation from the experiments of our quoted paper, we obtain the following results. In the following table the first line gives the P.D. of a chain consisting of 0,1 M. HCl on the one side and of a 0,1 M. solution of the given electrolyte on the other side. The second line gives the logarithm of the proportion of the mobility of H· and of the other cation, the third line gives the proportion of this mobility itself.

Series A.

	HCl against			
	KCl	NaCl	LiCl	RbCl
P.D. (millivolts).	93	140	165	87
$\log \dfrac{u_H}{u_{cation}}$	1,63	2,46	2,90	1,29
$\dfrac{u_H}{u_{cation}}$	42,5	288	894	19,5

In the same manner the following table gives the results in chains with 0.1 M KCl solution as the one electrolyte and various other electrolytes in the same concentration:

Series B.

	KCl against				
	NaCl	LiCl	RbCl	Strychnine.	Atropine.
P.D. (millivolts).	48	74	8,5	35	40
$\log \dfrac{u_{K}{}^{\cdot}}{u_{cation}}$	0,84	1,29	−0,15	0,61	0,70
$\dfrac{u_{K}{}^{\cdot}}{u_{cation}}$	6,9	19,5	0,71	4,0	5,0

From these data we may construct the following table:

	From Series A.	From Series B.
$\dfrac{u_{H}}{u_{K}}$	42,5	
$\dfrac{u_{H}}{u_{Na}}$	288	
$\dfrac{u_{H}}{u_{Li}}$	894	
$\dfrac{u_{K}}{u_{Li}}$	21	20
$\dfrac{u_{K}}{u_{Na}}$	6,9	6,9
$\dfrac{u_{K}}{u_{Rb}}$	0,5	0,7
$\dfrac{u_{Na}}{u_{Li}}$	3	3

The figures of the first and the second column are in good agreement in spite of the very different experimental conditions. Let us take

the mobility of K˙ as 1 and calculate the relative mobilities of the other cations from the figures of the first column, we obtain:

	Li	Na	K	Rb	H
Relative mobility in the membrane.........	0,048	0,145	1	2,8	42,5
" " " free aqueous solution....	0,52	0,65	1	1,04	4,9

The series of the mobilities of the ions in the membrane is quite the same as in a free aqueous solution, but the differences of the mobilities are enormously exaggerated in the membrane. The differences are so large that the K˙ ions may be considered as almost impermeable in comparison with the H˙ ion; on the other hand the Na˙ ion, and still more the Li˙ ion, as almost impermeable in comparison to the K˙ ion. This behavior recalls certain elective permeabilities in physiological membranes. A membrane which appears to be quite permeable for K˙ ions in the usual time of a physiological experiment may appear impermeable for Na˙ ions under the same conditions.

15. Hitherto we have completely neglected the penetration of the anions into the collodion membrane. As mentioned above this assumption may be only relatively justified. Let us try to calculate the real permeability of the anions. For this purpose let us first consider the concentration chain with 0,1 and 0,01 KCl and treat it by the theory for *permeable* membranes and calculate the ratio of the mobilities of K˙ and Cl'. The figures are not reliable enough for an exact calculation since an error of 1 millivolt has a great influence on the calculated relative mobilities if the P.D. of the chain be only little smaller than the possible maximum value of 57 millivolts. However, in any event, we may assert that the high value of the P.D. of this chain can only be explained if we assume the mobility of Cl' to be *at least* one-tenth of that of K˙. But since the mobility of K˙ is about twenty times as great as that of Li˙, the concentration chain with LiCl should show under these conditions almost no P.D. or even a P.D. of inversed sign. However, the P.D. of the LiCl concentration chain is as great as the one of the KCl chain. Therefore we should assume the mobility of Cl' to be at least one-tenth of that of Li˙, and that means $\frac{5}{1000}$ of the mobility of K˙. Really, the mobility of Cl' may be much smaller.

Another case allows us to calculate the mobility of OH′ ion approximately in comparison with that of Cl′. Let us consider the chain KCl-KOH and the chain NaCl-NaOH. In these chains only the difference in the mobilities of OH′ and Cl′ can be the cause of the electromotive effect. The chain KCl-KOH in 0,1 M concentration gives a P.D. from 5 to 13 millivolts, KCl being negative; in 0,01 M concentration the P.D. is practically zero. This shows that the difference in the mobilities of Cl′ and OH′ must be very small. However this conclusion is only justified under the condition that the mobilities of these anions are great enough to produce a well defined condition of concentration in the membrane and a well defined P.D. There is another possibility for the interpretation of these chains. Possibly the permeability of all these anions is so extremely small that a well defined influence on the potential does not take place. This explanation seems to be the more probable and we may conclude that most samples of completely dried up collodion bags are practically impermeable for any anion.

16. A similar situation may exist in the case of the bivalent cations Ca″, Mg″, and Ba″. As we showed in our quoted paper, concentration chains with the chlorides of any of these cations in collodion membranes give very small and uncertain P.D.'s which do not even agree with each other as to the sign of charge, and fluctuate with the time. It may be that the bivalent anions are still slower than Li˙, moving at such a rate as no longer to give definite potentials. This fact is remarkable because in free aqueous solutions the mobility of the bivalent cations generally is not smaller than that of the univalent cations. Furthermore it is remarkable that the trivalent cations Al‴ and Ce‴ give much better defined potentials than the bivalent cations, and about the expected value, viz. one-third of the value of concentration chains with univalent cations. We may summarize the general results in the following manner. The H˙ ion penetrates the collodion membrane more rapidly than other cations, then follow the other univalent cations in the same series as for free diffusion in aqueous solution, but the differences in mobility are much greater in the membrane. Bivalent cations are so little permeable as not to allow well defined measurements, trivalent cations penetrate better though exact figures cannot be calculated.

SUMMARY.

From experiments on such membranes as apple skin, parchment paper membrane, and a membrane of completely dry collodion, results have been obtained which could be interpreted by the assumption that these membranes are less permeable for anions than for cations. In parchment paper there is only a relative diminution of the mobility of the anions, in the apple skin and in the dry collodion membrane there is practically no permeability for anions at all. The theory is developed which explains how the decrease or complete lack of mobility of anions influences the electromotive effects of the membrane and the diffusibility of electrolytes across a membrane. The results of the theory are compared with the experimental results.

In membranes impermeable for anions the permeability for cations gives the same order of cations as for the mobilities in a free aqueous solution. But the differences of the mobilities are enormously magnified, e.g. the mobilities of H˙ and Li˙, which are in the proportion of about 1:10 in aqueous solution, are in proportion of about 1:900 in the collodion membrane. The general cause for the retardation of ionic mobility within the membrane may be supposed to be the increased friction of the water envelope dragged along by the ion in the capillary canals of the membrane. The difference of the effect on the cations and on the anions may be attributed to the electric charge of the walls of the canals.